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Growth of Copper Sulfate Pentahydrate Single Crystals by Slow Evaporation Technique

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ABSTRACT

Single crystals of $CuSO_4.5H_2O$ (CSP) were grown by slow evaporation solution technique at room temperature from its aqueous solution with molarity (0.25, 0.5 and 1.5) M. The sizes of the crystals were up to (39×12×3) mm^3, (33.05×30.5×4.7) mm^3 and (19.12×15.3×5.5) mm^3 respectively. XRD patterns were recorded for powder of single crystals to find the parameters of crystals. FTIR studies confirm the presence of various functional groups in the crystals. The optical absorption was study by using UV-Vis analysis. The spectra show low absorbance in the range between 300 nm and 550 nm. Energy gap (E_g) of crystals was found to be (4.17, 4.19 and 4.25) eV at the molarity of (0.25, 0.5 and 1.5) M respectively.

Indexing terms/Keywords

$CuSO_4.5H_2O$, single crystals, slow evaporation, XRD, FTIR, UV-Vis

Academic Discipline and Sub-Disciplines

Physics, Material Science

1. INTRODUCTION

Growth of crystals is the basis for many technological developments and the solution method is a very important process because it's used in many applications and industry [1,2]. Solid bodies in which the elementary building blocks are arranged regularly in the space lattice with specific geometrical symmetry are called crystals [3]. The kinetics of crystal growth and nucleation in connection with the quantity of material available for growth of crystal determine the produced of number and volume of the crystals [4]. The pentahydrate form of copper sulfate ($CuSO_4 \cdot 5H_2O$) is a bright blue in colour belonging to the space group C_i^1 and it has triclinic system [5,6]. The single crystal of copper sulfate is used as broadband UV optical filters by Manomenova et al. in (2013) [7]. The aim of this paper is to give report about the growth of copper sulfate (CSP) single crystals with different molarities by slow evaporation method. The XRD diffraction and FTIR spectral analysis for the powdered samples are used to identify the structural properties of single crystals. The grown crystals are polished to thickness of (2 mm) to record the optical absorption.

2. Experimental

$CuSO_4.5H_2O$ powder provided by [BDH Chemicals Ltd Poole England] with "minimum assay (ex Cu) 98.5%, maximum limits of impurities, Alkalis (sulphated) 0.5%, Chloride (Cl) 0.005%, Iron (Fe) 0.08%", is used to grow $CuSO_4.5H_2SO_4$ single crystals by slow evaporation method with molarities of 0.25, 0.5 and 1.5 M using double distilled water as a solvent. The mixture of distilled water and CSP salt at different molarities is placed in a magnetic stirrer and mixed up well to get homogenous solution. The solution was filtered using filter paper and allowed for slow evaporation at room temperature. The good quality crystals were collected after 82, 91 and 42 days for molarities 0.25, 0.5 and 1.5 M respectively. The grown crystals are shown in Fig. 1. The starting of nucleation, the time of growth and the size of these crystals are shown in the table (1).

Fig. 1: As grown crystals of (CSP).

Table 1: Time of crystallization and size of crystals.

Molarity of solution (M)	The time of the beginning of nucleation (days)	The time of completion of crystal (days)	The size of large crystal (mm^3)
0.25	78	82	39×12×3
0.5	76	91	33.5×30.5×4.7
1.5	2	42	19.12×11.38×8

3. Results and Discussion

X-ray Diffraction Analysis

The powdered forms of the grown crystals were subjected to powder X-ray diffraction analysis. The X-ray diffraction data were recorded using "XRD 6000" which has the properties, "Source: Cu kα, Wavelength 1.5406 Å, Scan model continues scan, range (10-50) degrees". The recorded PXRD patterns of (CSP) are shown in Fig. 2. The parameters of unit cell are in agreement with the (ICDD) card number 11-0646. The narrow peaks in the XRD patterns show the good quality crystalline nature of the grown crystals [8]. The highest peak of the samples occurs at 2θ~ 18° which is referred to $(0\bar{1}1)$ plane. From Fig. 2, it is clear that the increase in the molarity leads to a change in the intensity of peaks when compared with each other because the planes of particles in the powder are not aligned so the reflections intensities were not equal in all direction [9]. From PXRD diffraction analysis, it has been confirmed that the grown crystals belong to triclinic system. The comparison of the cell parameter values of crystals is shown in table (2).

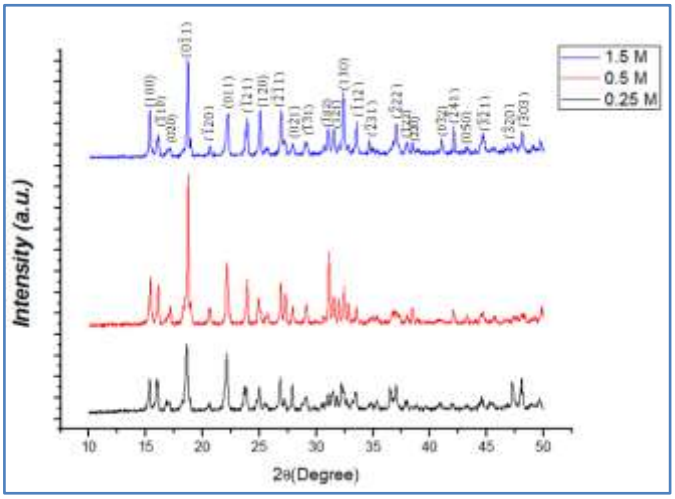

Fig. 2: PXRD patterns of grown crystals.

Table 2: Unit cell parameters for samples of crystals grown at room temperature.

Lattica Parameters	Molarity (M)			Standard
	0.25	0.5	1.5	11-0646
a(Å)	7.156	7.174	7.250	7.155
b(Å)	10.28	10.74	10.88	10.71
c(Å)	5.9084	5.9625	6.092	5.955
α (deg.)	96.50	97.48	98.07	97.63
β (deg.)	124.8	125.3	125.5	125.3
γ (deg.)	94.41	94.46	94.20	94.32

FTIR Analysis

The FTIR analysis of (CSP) single crystals were carried out using "IR Affinity-1" spectrophotometer by "KBr" pellet method in the wave number range of (400 to 4000 cm^{-1}). The transmittance spectra of the grown crystals are shown in Fig. 3. The

O-H stretching absorption bands appears at 3446 cm^{-1}, 3448 cm^{-1} and 3344 cm^{-1} for molarities 0.25, 0.5 and 1.5 M respectively [10]. Bending vibration of O-H appears at 1629 cm^{-1}, 1625 cm^{-1} and 1633 cm^{-1} for the molarities 0.25, 0.5, 1 and 1.5 M respectively [11]. The Stretching vibration of S-O group appears at 1151 cm^{-1}, 1151 cm^{-1} and 1209 cm^{-1} for molarities 0.25, 0.5 and 1.5 M respectively. The SO_4 non-degenerate mode appears at 997 cm^{-1}, 995 cm^{-1} and 997 cm^{-1} for molarity 0.25, 0.5 and 1.5 M [12]. The Vibration mode of metal ion Cu^{+2} (Cu-O-H) appears at the 785 cm^{-1}, 785 cm^{-1} and 786 cm^{-1} for 0.25, 0.5 and 1.5 M respectively [13]. The SO_4 degenerate mode appears at the 659 cm^{-1}, 659 cm^{-1} and 657 cm^{-1} for molarities 0.25, 0.5 and 1.5 M respectively [14]. The SO_4^{-2} bending group of sulfate appears at 453 cm^{-1}, 451 cm^{-1} and 516 cm^{-1} for the molarities 0.25, 0.5 and 1.5 respectively [11].

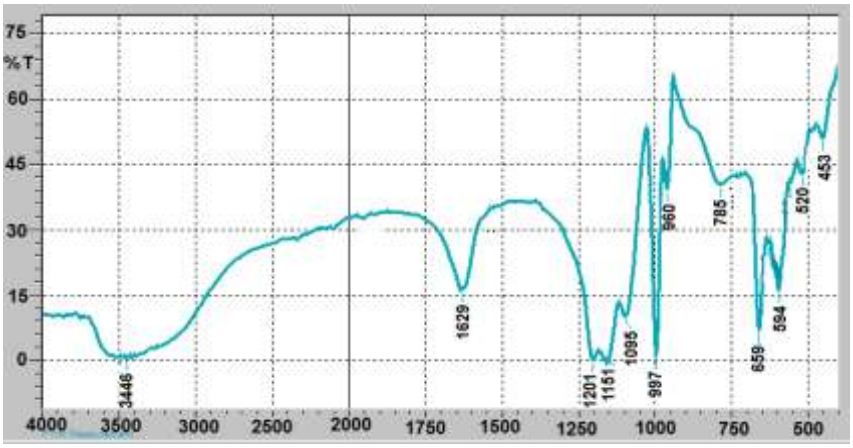

Fig. 3: FTIR transmittance spectrum of (0.25 M) crystal.

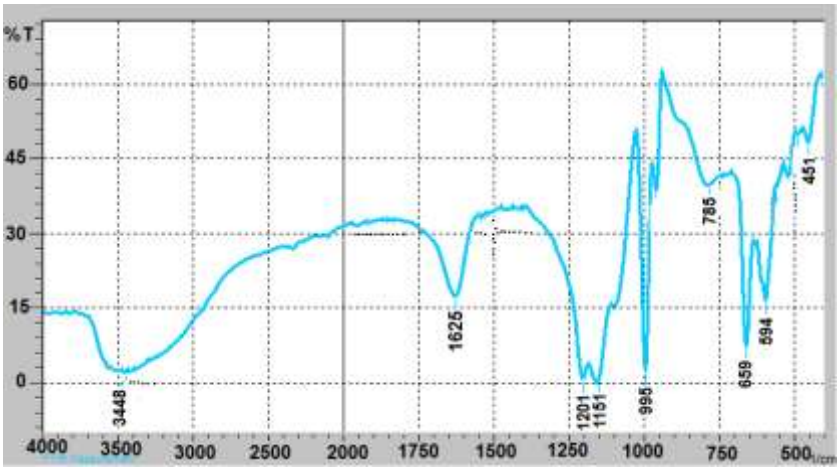

Fig. 4: FTIR transmittance spectrum of (0.5 M) crystal.

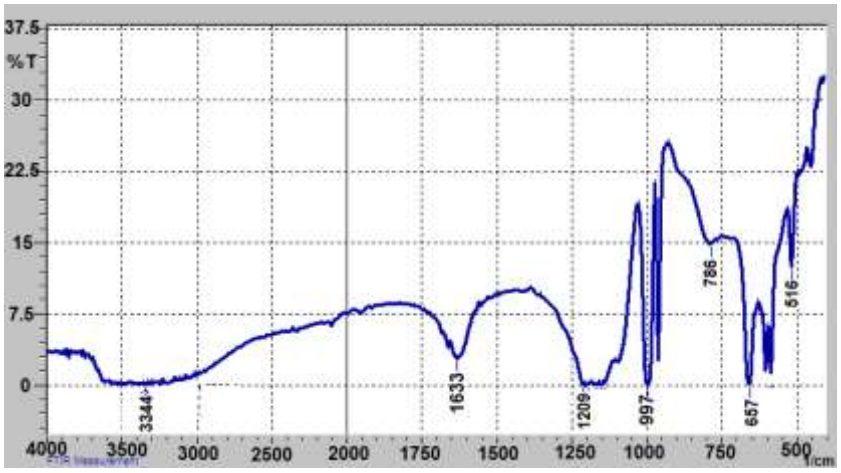

Fig. 5: FTIR transmittance spectrum of (1.5 M) crystal.

The difference in appearance of modes of ions (SO_4^{-2}) is attributed to the chemical reactivity of copper salts on KBr windows [15]. From table (3) it is clearly seen that all bands shift to higher or lower wavenumbers with changing the

molarity and this can be attributed to the external factors such that impurities, temperature and pressure during growth of crystals.

Table 3: IR bands of CSP grown crystals.

Wave number (cm^{-1})			Assignment
0.25 M	**0.5 M**	**1.5 M**	
3446	3448	3344	O-H stretching
1629	1625	1633	O-H bending
1151	1151	1209	S-O Stretching
997	995	997	SO_4 non-degenerate mode
785	785	786	Cu-O-H Vibration mode
659	659	657	SO_4 degenerate mod
453	451	516	SO_4^{-2} bending group of sulfate

UV-Vis Spectral Analysis

UV-Visible absorption spectra of (CSP) crystals were recorded by using "UV–Visible 1800 Double beam spectrophotometer" in the range of 200-800 nm. The crystals of CSP were cut and polished into plates. The spectra are shown in Fig. 4. Information about the electronic structure of the molecules can be extracted from UV-Visble spectra due to promotion of the electrons from the ground state to higher states [16]. From the UV-Visible spectra for the crystals of (CSP) it is noticed that the absorbance does not exceed two units in the entire visible region. The absorbance increases with decreasing the molarity. There is an abnormal absorption peak at ~340 nm that may be belong to distorted CuO_6 octahedron because the copper ion Cu^{+2} in the electronic configuration d^9 exhibits the Jahn-Teller effect [17]. The spectra show low absorbance in the visible region but higth absorbance in the infrared region and the ultraviolet region (~ 200-290) nm, this is in agreement with the results reported by Anne et al. [13]. The (CSP) crystals is transparent in the wavelength range between 300 nm and 530 nm and it can be used as optical bandpass filters in this range, this result is in agreement with the results reported by Manomenova et al. [7] and Anne et al. [13]. The indirect band gap value of (CSP) crystals can be found by plotting $(\alpha h\nu)^{1/2}$ versus $(h\nu)$. The energy gap was found to be 4.17, 4.19 and 4.25 eV for the molarities 0.25, 0.5 and 1.5 M respectively [4,13]. The energy gap plots are shown in Fig. 5.

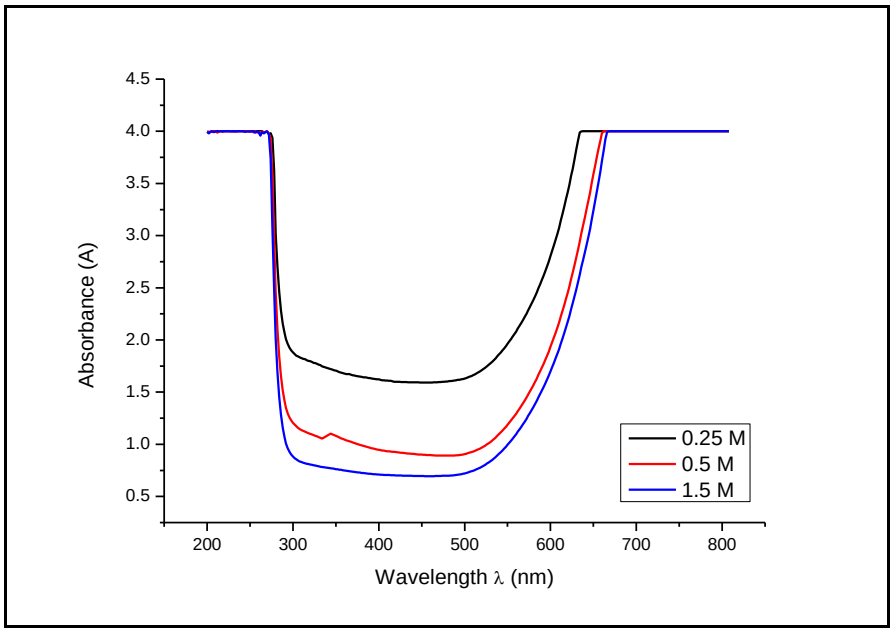

Fig. 4: Absorbance (A) versus wavelength (λ) of (CSP) single crystal.

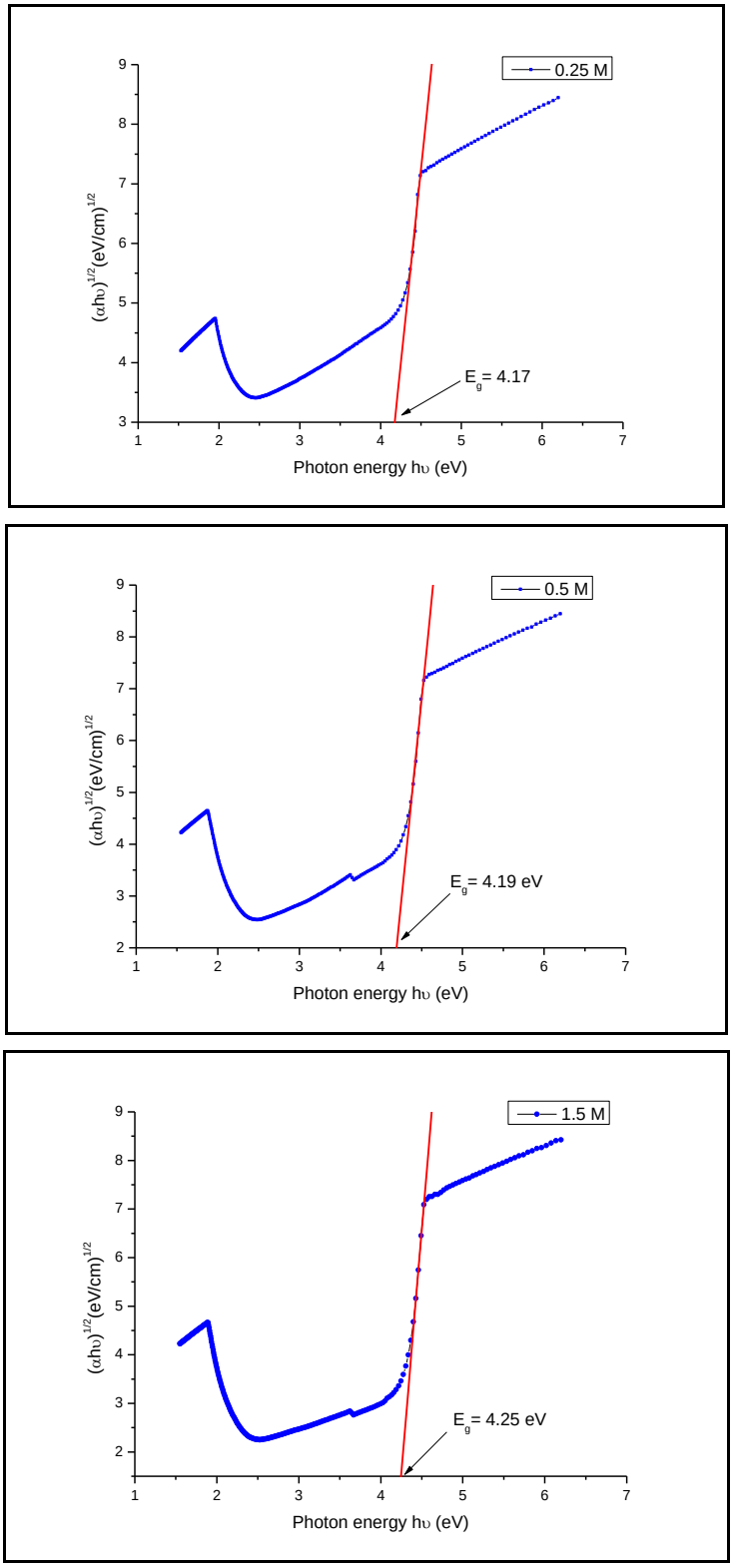

Fig. 5: The relation between $(\alpha h\upsilon)^{1/2}$ and $(h\upsilon)$ of (CSP) single crystals.

Conclusion

Single crystals of (CSP) were grown by slow evaporation process with solution molarities 0.25, 0.5 and 1.5 M. The slowest crystallization process occurs at solution molarity of 0.5 M where the time needed for completion of crystallization process was 91 days producing the largest crystal size of 33.5×30.5×4.7 mm^3. X- ray diffraction analysis is conducted on CSP crystals using the powdered pattern. The PXRD diffraction analysis revealed that the crystals belong to triclinic system. It is noticed that the highest peak of the samples occurs at 2θ~ 18° which is referred to $(0\bar{1}1)$ plane. The vibrational modes of

functional groups were identified using FTIR spectroscopic technique. The UV-Vis spectral study highlights the excellent transparency of the crystal in the entire visible region. Energy gap (E_g) of crystals is found to be 4.17, 4.19 and 4.25 eV at the molarities 0.25, 0.5 and 1.5 M respectively. The (CSP) crystals can be used as optical bandpass filters.

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